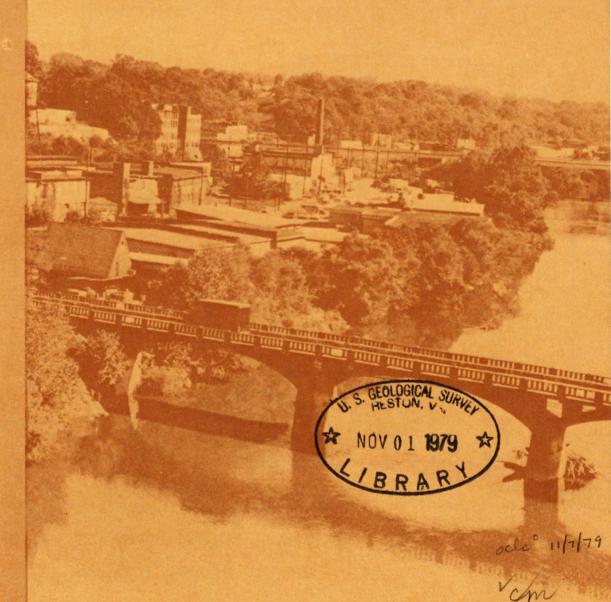


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WATER QUALITY OF THE FRENCH BROAD RIVER, NORTH CAROLINA

An analysis of data collected at Marshall, 1958-77

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U. S. GEOLOGICAL SURVEY
WATER RESOURCES INVESTIGATIONS 79-87

PREPARED IN COOPERATION WITH THE NORTH CAROLINA DEPARTMENT OF NATURAL RESOURCES AND COMMUNITY DEVELOPMENT

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16. Abstracts

An investigation of water quality in the industrialized French Broad River basin of western North Carolina has identified water-quality variations, the extent of man's influence on water quality, and trends in changes in the chemical quality of the river. The study centered on data collected during 1958-77 at the U.S. Geological Survey's station at Marshall, N.C.

The French Broad is a clean river. Only occasionally have concentrations of some trace metals been observed to exceed drinking water standards. However, 58 percent of samples analyzed for fecal coliform bacteria during 1974-77 exceeded criteria levels for bathing waters.

Most water-quality variations are associated with variations in streamflow. Concentrations of constituents transported in solution generally decrease at higher flows, whereas concentrations of materials associated with suspended sediment increase with flow. No correlation between discharge and nutrient concentrations has been observed.

Man's activities in the basin have resulted in deterioration of water quality. In 1958, an estimated 64 percent of the inorganic dissolved-solids load in the river at Marshall was due to man-made pollution, and by 1966, it was 74 percent. As of 1977, water quality had returned to levels of 1958, apparently the result of new waste-water treatment facilities and improved industrial technology.

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WATER QUALITY OF THE FRENCH BROAD RIVER, NORTH CAROLINA

An analysis of data collected at Marshall, 1958-77

Ву

C. C. Daniel III, H. B. Wilder and M. S. Weiner

U.S. GEOLOGICAL SURVEY WATER-RESOURCES INVESTIGATIONS 79-87



Prepared in cooperation with the

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COVER PHOTOGRAPH: Water, industry, mountains—the French Broad River at Asheville. Photograph courtesy of the Asheville, North Carolina Citizen-Times.

INTERNATIONAL SYSTEM UNITS

The following factors may be used to convert the U.S. Customary units published herein to the International System of Units (SI).

Multiply U.S. Customary uni	lts By	To obtain SI units
	Length	
<pre>inches (in) feet (ft) miles (mi)</pre>	25.4 .3048 1.609	millimeters (mm) meters (m) kilometers (km)
	Area	
acres square miles (mi ²)	.4047 .004047 2.590	square meters (m ²) hectares (ha) square kilometers (km ²) square kilometers (km ²)
square miles (mi)	2.390	square kilometers (km)
	Volume	
million gallons (10 ⁶ gal) acre-feet	3.785 .003785 3785 1233.5	liters (L) cubic meters (m ₃) cubic meters (m ₃) cubic meters (m ₃)
cubic feet (ft ³)	.02832	cubic meters (m ³)
	<u>Flow</u>	
cubic feet per second (ft 3/s)	28.32	liters per second (L/s)
million gallons per day (Mgal/d)	.02832 .04381	cubic meters per second (m_3^3/s) cubic meters per second (m_3^3/s)
gallons/day (gal/d)	.0038	cubic meters per day (m ³ /d)
	Temperature	
degree Fahrenheit (°F)	5/9(°F-32)	degree Celsius (°C)
	Mass	
ton (short, 2000 pounds) pound (1b avoirdupois)	907.2 .4536	kilograms (kg) kilograms (kg)

WATER QUALITY OF THE FRENCH BROAD RIVER, NORTH CAROLINA

An analysis of data collected at Marshall, 1958-77

By C. C. Daniel III, H. B. Wilder and M. S. Weiner

ABSTRACT

An investigation of water quality in the French Broad River in North Carolina has resulted in the definition of variations in water quality, a determination of the degree to which the quality of water in the river has been affected by man's activities and, an analysis of trends in the changing chemical quality of the river. This investigation centers on data collected during 1958-77 at the U.S. Geological Survey's station at Marshall, N.C.

The French Broad River drains 1,667 square miles of the Blue Ridge Mountains Province in western North Carolina. The river basin is the most industrialized basin in the mountain region of the State, with 30 percent of the employed population engaged in manufacturing. Between 1940 and 1970 the total population upstream from Marshall increased by 40 percent to 218,000 inhabitants.

The quality of water in the French Broad River at Marshall is suitable for most uses. None of the major dissolved constituents and nutrients, nor defined properties such as hardness, alkalinity and color, exceed suggested limits for drinking waters. Chromium, lead, selenium, and zinc are the only trace metals to occasionally exceed drinking-water standards. Dissolved oxygen levels are high year round, remaining near or above the saturation level even at higher summer temperatures. Results of tests for biological oxygen demand and chemical oxygen demand characterize the French Broad at Marshall as a clean river. However, fifty-eight percent of samples analyzed for fecal-coliform bacteria during 1974-77 exceeded recommended limits for bathing waters.

Most water-quality variations are associated with variations in streamflow. The variation of specific conductance with streamflow follows a non-linear, inverse relation. Similarly, concentrations of constituents transported primarily in solution generally decrease at higher flows, whereas concentrations of materials that tend to be associated with suspended sediment increase with flow. Most trace metals clearly tend to be transported in association with suspended sediment. At the low concentrations measured, the mode of transportation for arsenic, cadmium, selenium, and mercury is not clearly defined. Arsenic and mercury are apparently carried in solution, selenium seems to be mostly in solution, and cadmium appears to be associated with the sediment. No demonstrable correlation between stream discharge and nutrient concentrations has been observed.

Man's activities in the basin have resulted in deterioration of water quality in the French Broad River. In 1958, an estimated 64 percent of the dissolved solids load in the river at Marshall was due to pollution. By 1966, 74 percent of the dissolved load could be attributed to pollution. Loads of dissolved solids, sodium, sulfate, and calcium showed the most dramatic increases, coinciding with general increases in population and industrial employment. Perhaps as early as 1967, but certainly since 1974 the amount of inorganic constituents has decreased dramatically in spite of increased population and industrial growth. New waste-water treatment facilities and improved industrial technology have apparently combined to curb pollution and reverse the earlier trend. In 1977 water quality had returned at least to levels of 1958.

INTRODUCTION

This report presents the results of an investigation of the quality of water in the French Broad River at Marshall, N.C., that is based on data collected during the period 1958-77. Major objectives of the study were: (1) to define variations in water quality; (2) to determine the degree to which the quality of water in the river is affected by man's activities; and, (3) to identify past and present trends in the chemical quality of water in the river. This investigation was made by the U.S. Geological Survey in cooperation with the Environmental Management Division of the North Carolina Department of Natural Resources and Community Development.

The water-quality program, of which this study is a part, is explained in the report, <u>Program for Evaluating Stream Quality in North Carolina</u>, by H. B. Wilder and C. E. Simmons (1978).

Water-quality data were collected on a daily basis at Marshall from 1958-67 as part of a statewide survey of the chemical quality of surface waters of the State. Collection of data was resumed at Marshall from 1973-77 as part of a new program to collect additional information on

water quality, and to evaluate the effects of man's activities on the quality of waters in North Carolina's major rivers. Including the station at Marshall, there are a total of nine sites in the French Broad River basin where daily samples have been collected for a period of one year or more; these are shown in figure 1. A summary of data-collection activities at these sites is presented in figure 2 and data from these as well as other stations in the basin are summarized in Wilder and Slack (1971).

In addition to the data collected for this study, the North Carolina Department of Natural Resources and Community Development maintains a network of 81 stations in the basin to monitor water quality at sites known to be affected by specific sources of pollution (North Carolina Environmental Management Commission, 1976).

The authors also acknowledge critical reviews by David H. Howells, former Director of the Water Resources Research Institute of the University of North Carolina, and Roy M. Davis, North Carolina Department of Natural Resources and Community Development, that added significantly to the accuracy of this report.

BASIN CHARACTERISTICS

Physical Setting

The French Broad River flows from its headwaters on the North Carolina-South Carolina state line northward across the state into Tennessee. Upon entering Tennessee the river turns to flow in a westwardly direction, into Douglas Lake, and from there on to Knoxville where it joins the Holston River to become the Tennessee River.

In North Carolina, the French Broad River drains 1,667 mi² (square miles) of which 1,332 mi² are upstream from the station at Marshall. Marshall is the most downstream site in North Carolina at which both streamflow and daily water-quality data were collected during the most recent phase of the study. The drainage area lies within the Blue Ridge Mountains Province and includes all of Buncombe, Henderson, Madison, and Transylvania Counties and a very small part of Haywood County, near Canton. (See figure 1.) The average altitude of the basin within North Carolina is between 2,500 and 3,000 feet above msl (mean sea level), but altitudes range from 6,419 feet along the drainage divide on the Buncombe-Yancey County line to 1,240 feet where the river enters Tennessee.

From its headwaters near Rosman, the French Broad River flows northeastward in a broad valley to its confluence with the Mills River near Fletcher. Downstream from this confluence the river course changes to a more north-northwesterly direction and the valley narrows. It is in this reach that the French Broad is joined by the Swannanoa River at Asheville. Although the topography of the basin is generally mountainous, Asheville lies in a central intermontane valley of moderate relief.

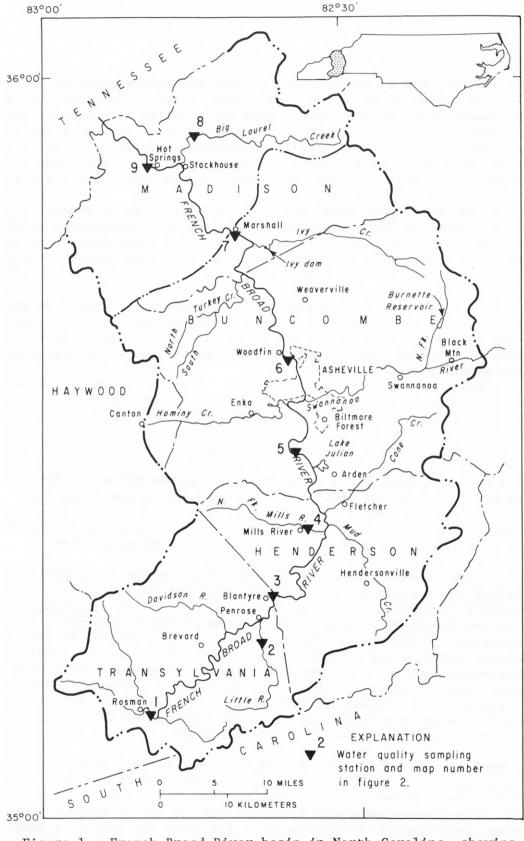


Figure 1.—French Broad River basin in North Carolina, showing stations where water samples have been collected for one year or more, and the drainage area upstream from the station at Marshall, N.C.

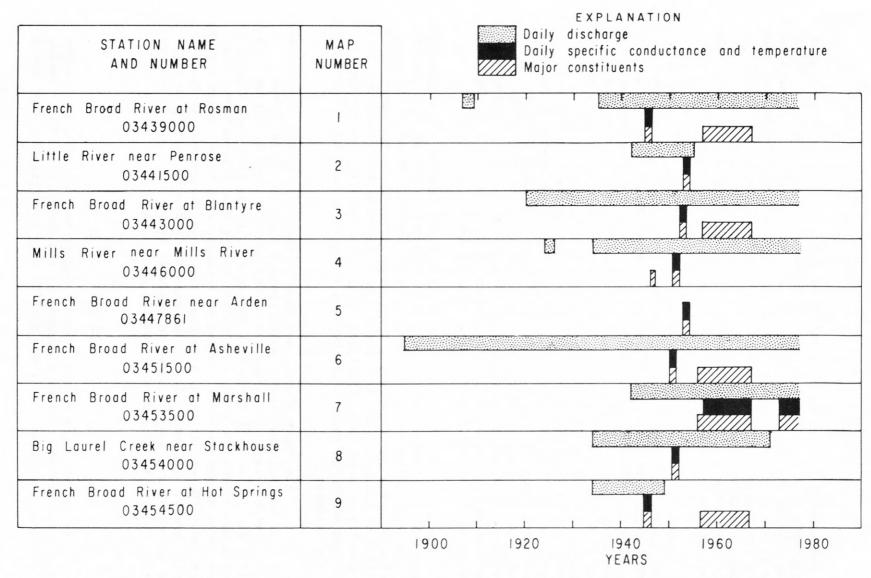


Figure 2.—Period of data collection at stations in the French Broad River basin where daily data have been collected for one or more years.

Beyond Asheville, the French Broad River flows through the most rugged topography in the basin as it cuts through the core of the Appalachian Mountains in the Great Smoky Mountains region. Northwest of Asheville the French Broad is joined by Ivy Creek, approximately 2 miles upstream from the Geological Survey station at Marshall. The average stream gradient between Rosman and the Mills River is only about 3 feet per mile. From the Mills River confluence to the Tennessee state line, the gradient steepens to an average of about 12 feet per mile.

Although there are numerous ponds and lakes in the French Broad River basin, only three have a gross capacity equal to or exceeding 9,000 ac-ft (acre-feet). Lake Julian, upstream from Asheville, with a capacity of 9,000 ac-ft, is a cooling lake for a power company steam generating plant. Burnett Lake, in Buncombe County, has a capacity of over 23,000 ac-ft and serves as part of Asheville's municipal water supply. Ivy dam on Ivy Creek in Madison County, is owned by TVA (Tennessee Valley Authority) and forms a lake with a gross capacity of 43,600 ac-ft. The proposed Turkey Creek dam, to be located in Buncombe County and built by TVA, would form a lake with a gross capacity of 45,000 ac-ft. Because of the relatively small capacities of these existing and proposed reservoirs and their distances upstream from the sampling site at Marshall, their effects on the quantity and quality of streamflow at Marshall are probably negligible.

The basin is underlain by sparingly soluble igneous and metamorphic rocks that at shallow depths are characteristically broken by a network of fractures. These fractures may, in some places, extend downward to depths of a few hundred feet, but are most prevalent in the upper 25 to 50 feet of bedrock. Bedrock on the upper slopes of the ridges and peaks is usually covered by a thin layer of granular material in the form of soil and weathered rock, which becomes thicker on the lower slopes and in the valleys.

Most of the upper slopes, and many of the lower slopes, are covered with well-established forests which protect the land surface from erosion with a layer of fallen leaves and decaying organic matter. The valley floors, as well as much of the lower slopes, have been cleared of forest cover; and are under cultivation or are used for pasture. However, most of the basin is covered by forests, with forest cover ranging from about 70 percent in Madison County to about 90 percent in Transylvania County. The remainder of the area is devoted primarily to crop and pasture land; but, as shown in table 1, there are significant population centers in each of the counties in the basin.

Climate

Climate, which is strongly influenced by the mountainous topography, is the primary control of runoff in the French Broad River basin. In general, the higher altitudes receive more precipitation and have a

Table 1.--Population data for the four principal counties and their major municipalities in the French Broad River basin

County/largest town	^a 1940	^a 1950	^a 1960	^b 1970	c 1976 (estimated)
Buncombe/Asheville	109,000	124,000	129,000	145,000	151,000
Henderson/Hendersonville	26,000	31,000	33,000	43,000	49,000
Madison/Marshall	22,000	20,000	17,000	16,000	17,000
Transylvania/Brevard	3,100	3,900	15,000	20,000	21,000

^aU.S. Bureau of the Census, 1963.

^bU.S. Bureau of the Census, 1971.

 $^{^{}m C}$ North Carolina Division of State Budget and Management, 1977.

lower mean annual air temperature than the lower altitudes. The area immediately around Asheville, which corresponds roughly to the center of the basin in North Carolina, has a mean annual temperature of 56°F, and mean daily range from 99°F to -7°F. The mean annual precipitation at Asheville is 38 inches, the lowest in North Carolina. Rosman, located in the upper headwaters in Transylvania County, has a mean annual precipitation of 77 inches, which is one of the highest in the State. On a seasonal basis, precipitation tends to be highest during winter and spring and lowest during summer and fall.

Streamflow in the French Broad River basin is derived from precipitation. Part of the precipitation falling on the land surface moves rapidly into streams either by running directly over the land surface as overland runoff or by moving through near-surface routes provided by the porous organic layer that blankets the land surface and by root holes, animal burrows, and other openings within a few feet of the land surface. Another part of the precipitation supports streamflow during dry periods by becoming ground-water recharge and percolating into the layer of weathered rock. bedrock fractures, and valley sediments. This ground water discharges slowly by seeping laterally into stream channels or to springs.

The seasonal variation of temperature is important in that it influences streamflow. An example is the low streamflow generally experienced in late summer and early fall. This is caused, in part, by the higher temperatures of summer, which increase evaporation and transpiration, thus reducing the water available for overland runoff and ground-water recharge.

The general decrease of temperature with increasing altitude is also an important factor in that it results in areal variations in evapotranspiration, and subsequently areal variations in streamflow. Because of generally lower temperatures at higher altitudes, the growing season is shorter than in nearby non-mountainous areas. Consequently, the loss of water due to evaporation and transpiration by plants is lower on an annual basis at higher altitudes than at lower altitudes, resulting in higher rates of runoff from the higher areas.

Population and Industrial Development

The French Broad River is the most industrialized river basin in the mountain region of the State with about 30 percent of the employed population engaged in the manufacture of textiles, pulp and paper, leather goods, furniture and other wood products. Based on the county-wide populations given in table 1, and prorated on the basis of the areas in each county drained by the French Broad, the population in the basin, above the sampling station at Marshall, is estimated to have been approximately 218,000 in 1970. This is an increase of 13 percent over the previous 10 years. In 1960, 41 percent of the inhabitants of the

area above Marshall lived in communities, while the remainder were classified as rural residents. By 1970, 37 percent of the population lived in communities and 63 percent lived in rural areas. It is interesting to note that even though the population of the four counties comprising the basin has increased 40 percent since 1940, the increase in population of the major urban areas (table 1) has been only 24 percent. The large population centers of Asheville, Hendersonville, and Brevard are also the major industrial centers. A few of the smaller towns, such as Enka and Pisgah Forest, support "single industries" large enough to have a significant effect on the water quality of the area.

Only about 8 percent of the employed population in the four-county area is engaged primarily in agriculture. An additional estimated 30 to 40 percent are part-time farmers or rural residents. Tobacco is the principal cash crop in Madison and Buncombe Counties, and apples are the principal crop in Henderson County. Dairy farming, swine, and poultry production are also important agricultural activities in the area.

Water Use and Waste Disposal

Water in the French Broad River system is treated and used by municipalities for drinking water and by private industry for various uses such as cooling in manufacturing processes. Major municipalities and industries discharging effluent into the French Broad River system are listed in table 2 (North Carolina Division of Environmental Management, 1976). Major is defined as any community or industry discharging 1.0 million gallons per day or more into the river system. Effluent is defined as used water and it is not necessarily polluted water in the sense that its quality characteristics have been changed by the use so that it contravenes State or Federal waste-water standards.

Of the communities and industries listed in table 2, the major point source of effluent in the upper end of the basin is a large chemical company, Olin Corporation; while in the lower part of the basin, the major point sources are a large synthetics plant, American Enka, and the waste water treatment facility for the Metropolitan Sewage District of Buncombe County. The sum of releases from municipal treatment facilities at smaller towns, such as Hendersonville and Brevard, and from some of the smaller industries in the basin represent a significant amount of effluents. Numerous nonpoint sources, such as agricultural operations and urban runoff, also affect stream quality.

The general increase in rural population and associated industrial growth coupled with a slower paced, but growing urbanization provides a basis for concern over the quality of water in the French Broad River basin. The following sections of this report will describe the quality of water in the French Broad River, as defined by the quality of water samples collected at Marshall, discuss its variability, the current status of pollution in the river, and the changes in quality that have

Table 2.--Sources of water supplies and points of waste disposal for municipalities and industries with waste-water discharges greater than 1.0 million gallons per day

Community or industry (location)	Source of water supply	Location of waste discharge	Water intake in millions of gallons per day	Volume of effluent in millions of gallons per day
Brevard (Transylvania Co.)	King Cr./Bushy Cr.	King Cr.	2.0	1.5
E. I. Dupont (Transylvania Co.)		Little River		2.0
Olin Corporation (Brevard)	Davidson R.	Davidson R.	26.5	27.3
Hendersonville Municipal (Henderson Co.)	Upper N. Fork Mills R./Bradley Cr.	Mud Creek	4.7	2.3
Cranston Print Works (Henderson Co.)	Cane Creek	French Broad R.	2.5	2.5
General Electric (Henderson Co.)	Hendersonville Water Dept.	Bat Fork Cr.	1.38	1.38
Metro-Buncombe Co. including:		French Broad R.		25.0
Asheville			22.5	combined
Biltmore Forest	Burnett Res.		0.25	discharge
Black Mt.			0.4	to Metro
Woodfin	Sugar Camp Fork Im- poundment/Laurel Fork		0.8	Sewage District
Weaverville	Ox Cr./Eller Cove		0.35)
American Enka (Buncombe Co.)	Hominy Cr.	Hominy Cr.	0.2 water dept. 8.0 Hominy Cr.	} 4.25
Carolina Power and Light	French Broad R./	French Broad/		2.0
Stream Station (Asheville)	Lake Julian	Lake Julian (any overflow goes to French Broad R.		4.0 re- cycles
Hedrick Sand and Gravel, Grove Stone and Sand Division (Swannanoa)	N. Fork Swannanoa R.	N. Fork Swannanoa R.	3.0	3.0

Sources of data:

- 1. North Carolina Environmental Management Commission, 1976.
- 2. U.S. Environmental Protection Agency, National Pollutant Discharge Elimination System (NPDES) permits.
- 3. Jackson, N. M., Jr., 1974.

accompanied the changes in population and industrialization over approximately the past 20 years.

WATER QUALITY

The quality of water in the French Broad River, as represented by samples taken at Marshall from 1974 to 1977, is satisfactory for most uses. None of the major dissolved constituents approach limits suggested for drinking waters (National Academy of Sciences, and National Academy of Engineering, 1972), and such defined properties as hardness, alkalinity, and color are all within acceptable ranges. The nutrients nitrogen and phosphorus were not observed to exceed drinking-water criteria, although they were sometimes present in amounts greater than recommended in eutrophication studies. Of the trace metals determined, chromium, lead, selenium, and zinc occasionally exceeded suggested limits for drinking water. Biologically the river met drinking water and aquatic environment criteria, except coliform bacteria were frequently far greater than the maximum limits recommended for bathing waters. Although there are no precise limits for allowable amounts of suspended sediment, it is likely that suspended matter is frequently high enough to interfere with fish propagation and other biological processes.

Variations in Water Quality

An understanding of the manner in which water quality varies is essential to its treatment and use. There are a number of important aspects of variation in water quality. Of the three most important, the most fundamental is a knowledge of the extremes within which constituents of interest to the user may be expected to range. Another is the correlation between changes in specific conductance and changes in the concentrations of various dissolved (ionized) water-quality constituents. A knowledge of relations between water-quality constituents and specific conductance can be an inexpensive and highly effective means of extending a small amount of data to a much longer period of record. third is the variation associated with changing streamflow, which is perhaps the single most important cause of water-quality variation. the French Broad River, as in most streams, concentrations of constituents transported primarily in solution generally decrease at higher flows, whereas concentrations of materials that tend to be associated with suspended sediment increase with flow.

Data from individual analyses of periodic samples collected from the French Broad River at Marshall during 1974-77 for some 96 water-quality characteristics are reported in individual annual data reports of the U.S. Geological Survey, entitled "Water Resources Data for North Carolina." Selected data are grouped, and ranges and averages, where applicable, are summarized in table 3 and several other tables in the following sections of this report.

Table 3.—Summary of chemical and biological constituents and physical properties of water in the French Broad River at Marshall, N.C., 1974-77 water years. (All units are milligrams per liter, except as noted.)

Major Dissolved Constituents	Number of samples	Range	Mean
Silica (SiO ₂)	36	3.7-11	8.7
Calcium (Ca)	36	3.2-10	5.2
Magnesium (Mg)	36	0.2-2.0	1.1
Sodium (Na)	36	2.4-22	7.8
Potassium (K)	36	1.0-2.9	1.6
Bicarbonate (HCO ₃)	39	9.0-35	18
Carbonate (CO ₃)	32	0.0-0.0	.0
Alkalinity (as CaCO ₃)	39	7.0-29	14
Sulfate (SO ₄)	36	5.1-42	14
Chloride (Cl)	36	0.9-5.8	3.3
Fluoride	36	0.0-1.2	.14
Dissolved solids (Residue at 180°C)	36	26-125	60
Dissolved solids (Sum of constituents)	36	30-112	52
Dissolved solids load (Tons per day)	36	176-3680	812
Hardness (as CaCO ₃)	36	11-32	18
Non-carbonate hardness (as CaCO ₃)	36	0.0-9.0	3.5
Dissolved oxygen (0 ₂)	133	7.3-15.4	9.8
Carbon Dioxide (CO ₂)	39	0.5-104	16

Table 3.—Summary of chemical and biological constituents and physical properties of water in the French Broad River at Marshall, N.C., 1974-77 water years. (All units are milligrams per liter, except as noted.)—Continued

Physical Characteristics	Number of samples	Range	Mean
Specific conductance (micromhos)	Once daily	33-205	86
pH (pH units)	39	5.2-7.8	
Temperature (°C)	Once daily	0.0-26.0	13.2
Color (platinum-cobalt units)	35	0.0-600	57
Turbidity (JTU)	14	6-64	
Biological Characteristics			
Total phytoplankton (cells per mL)	11	250-5,500	1,984
Periphyton biomass ash weight (gm/m^2)	10	.20-18	3.14
Periphyton biomass total dry weight (gm/m^2)	10	1.26-21	6.37
Total organic carbon (C)	30	3.0-44	11
Dissolved organic carbon (C)	27	2.5-20	6.6
Organic carbon in bed material (C) (gm/kg)	4	<0.1-6.7	
Methylene blue active substance	30	0.0-0.3	0.04
Chemical oxygen demand	95	10-56	
Biochemical oxygen demand, 5 day	101	0.2-4.9	1.9
Fecal coliform (colonies per 100 mL)	98	<10-12,000	11100

Log mean.

Major Dissolved Constituents

Concentrations of a number of significant constituents correlate sufficiently well with specific conductance so that, once a few concurrent measurements are made, concentrations of these constituents can be estimated with useful accuracy from a single measurement of conductance. For samples taken at Marshall, regression equations, correlation coefficients, and standard errors of estimate for the relation of major dissolved constituents to specific conductance are given in table 4. The regressions in table 4 are each based on no fewer than 264 data values; as a result, those regressions with correlation coefficients of 0.75 or greater are statistically valid at a significance level of better than 99 percent. Consequently, valid estimates of concentration can be expected from the equations given a measured value for specific conductance. Of the major dissolved constituents listed in table 4, sodium, sulfate, bicarbonate, and dissolved solids correlated well with specific conductance. An example of a good correlation is that between specific conductance and dissolved solids which is shown in figure 3.

The specific conductance of water in the French Broad River typically decreases as flow in the stream increases. The general characteristics of this non-linear inverse relationship are illustrated in figure 4. The concentrations of major chemical constituents having correlation coefficients greater than about 0.75 in table 4 can be expected to behave much like specific conductance in their relation to stream flow.

Suspended Sediment

Concentrations of suspended matter vary more with changes in streamflow than do materials in solution. Concentrations of suspended sediment, for example, have been observed to range from 3 mg/L (milligrams per liter) at a discharge of 1,020 ft 3 /s to 10,800 mg/L at a discharge of 17,600 ft 3 /s. The mean concentration for samples collected during the period 1974-77 was 926 mg/L.

As shown in figure 5, suspended-sediment concentrations tend to respond simultaneously with discharge. The general relation between discharge and suspended sediment is shown in figure 6. The line of regression of figure 6 has been used in conjunction with flow-duration data for 1974-77 to estimate the annual suspended-sediment yields shown in table 5. The average annual suspended-sediment yield during the four-year period was 750 tons per square mile per year. It is important to note that a calculation of average sediment concentration based on this figure of suspended sediment yield gives an estimated average

Table 4.—Summary of the results of the regression analyses relating the concentrations of dissolved chemical constituents to specific conductance, 1958-77 water years

Spec	ific	S	Dissolved chem	ical cor	stituents		Regression summa	ry	
Conduction (Micro at 2)		samples		Concent (milligrams				ion	error
Mean	Standard	Number of	Constituent	Mean	Range	Standard deviation	Simple regression equation	Correlation	Standard err of estimate (mg/L)
98	36	264	Dissolved Solids (DS) (sum of constituents)	65	30-145	22	$DS = 7.46 + 0.586 (SC)^{1}$	0.97	5.5
101	35	299	Calcium (Ca)	4.4	2.2-9.8	1.0	Ca = 2.53 + 0.0206 (SC)	.66	.60
98	36	299	Magnesium (Mg)	1.4	.20-2.9	.40	Mg = 0.976 + 0.00402 (SC)	.34	.40
98	35	300	Sodium (Na)	12	2.4-36	6.2	Na = -4.39 + 0.164 (SC)	.95	1.5
98	35	306	Chloride (C1)	4.0	.9-16	1.7	C1 = 0.631 + 0.0351 (SC)	.65	.13
97	35	297	Sulfate (SO ₄)	19	2.8-58	10	$SO_4 = -7.20 + 0.269$ (SC)	.93	3.0
98	36	289	Silica (SiO ₂)	11	3.2-14	1.4	$SiO_2 = 8.86 + 0.0174$ (SC)	.38	1.3
101	35	310	Bicarbonate (HCO3)	20	8.0-43	5.3	$HCO_3 = 7.53 + 0.124$ (SC)	.80	3.1
98	36	300	Potassium (K)	1.5	.20-3.9	1.6	K = 0.513 + 0.0104 (SC)	.24	1.6
98	36	272	Dissolved Solids (DS) (residue at 180°C)				DS = 11.0 + 0.606 (SC)	.94	6.2

 $^{^{1}\,\}mathrm{SC}$ is specific conductance.

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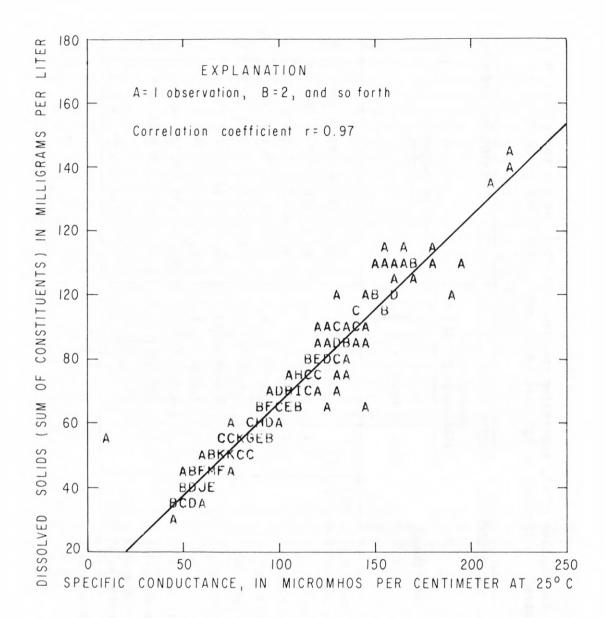


Figure 3.--Relation between specific conductance and dissolved solids, French Broad River at Marshall, N.C., 1958-77 water years.

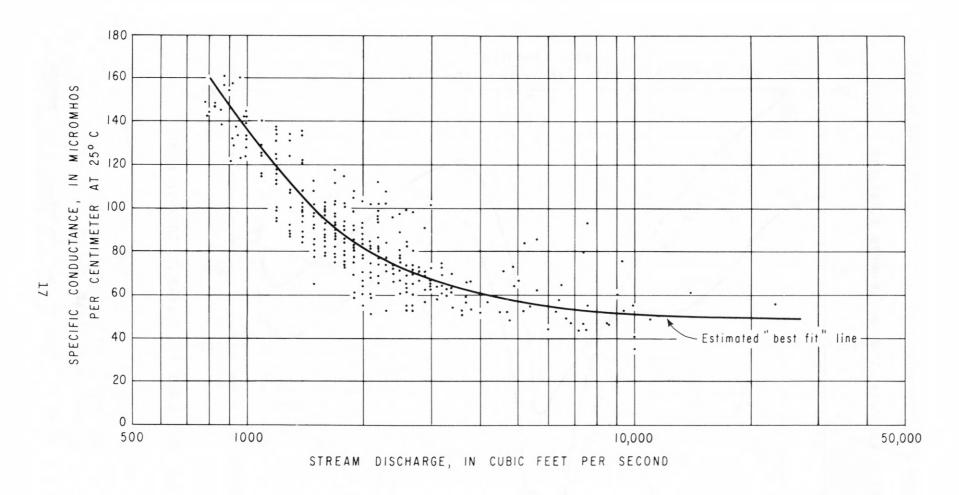


Figure 4.—Relation of specific conductance to discharge for the French Broad River at Marshall, N.C., 1977 water year.

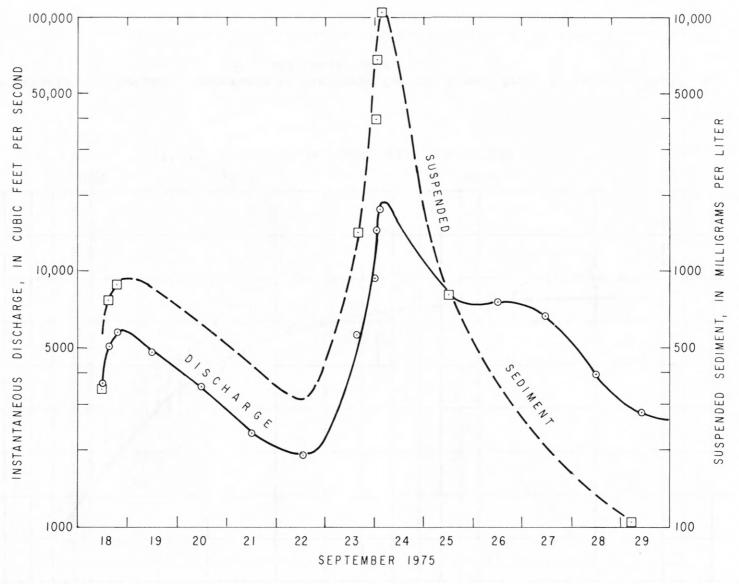


Figure 5.--A comparison of changes in suspended-sediment concentration and stream discharge with time, French Broad River at Marshall, N.C., September 18-29, 1957.

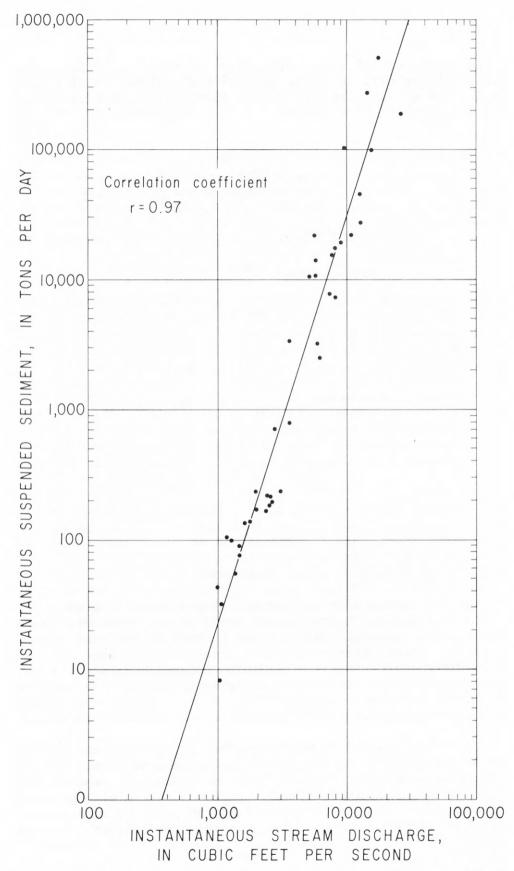


Figure 6.—Suspended-sediment transport curve for the French Broad River at Marshall, N.C., 1974-77 water years.

concentration of 347 mg/L. This value is much lower than the mean for actual samples (926 mg/L), suggesting that collection of sediment samples was somewhat biased towards periods of high flow.

Table 5.--Average suspended-sediment yield in the French Broad River at Marshall, N.C., 1974-77 water years

Water year(s)	Average suspended-sediment yield, in tons per square mile
1974	760
1975	989
1976	703
1977	550
1974-77	750

Nutrients

The nutrients, nitrogen and phosphorus, are not present in large amounts in the water in the French Broad River. However, even in small amounts, they are highly significant because they affect biological processes. Three types of criteria pertain to nutrient concentrations. One involves toxic effects of ammonia on freshwater aquatic life, another concerns drinking-water supplies and toxic effects of nitrate and nitrite on humans, and the third involves the role of excess nitrogen and phosphorus in eutrophication of surface-water bodies.

Depending upon the level of oxidation, nitrogen may occur in solution in water in one or more forms. The most common forms, in order of increasing stability in most aerated waters, are ammonia (NH $_3$), nitrite (NO $_2$), and nitrate (NO $_3$). Various organic nitrogen-bearing compounds are also common, particularly in polluted waters, but no attempt to identify these was made in this investigation. Because of

its toxicity to freshwater aquatic life, the U.S. Environmental Protection Agency (EPA) (1976) suggests a limitation of 0.02 mg/L of ammonia (as un-ionized ammonia, $\rm NH_3)$ for waters to be suitable for fish propogation.

Un-ionized ammonia is not measured directly but is calculated from the amount of dissolved ammonia. Ammonia gas and ammonium salts are quite soluble in water in the form of ammonium hydroxide. When ammonia dissolves in water, a chemical equilibrium is established that contains un-ionized ammonia (NH_3), ionized ammonia (NH_4), and hydroxyl ions (OH) according to the following simplified equation:

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

The equilibrium of this equation is dependent upon temperature and pH. Under prevailing conditions in the French Broad, at a mean temperature of 13°C , and mid-range pH of 6.5, the amount of un-ionized ammonia in aqueous solution is approximately 0.08 percent of dissolved ammonia (interpolated from table 3, EPA, 1976, p. 11). At a mean concentration of 0.10 mg/L dissolved ammonia (table 6) the un-ionized ammonia concentration is about 0.0001 mg/L, which is well below the recommended criteria level. On the other hand, if the most favorable conditions for ammonia (NH $_3$) formation were to occur simultaneously in the French Broad, with a pH of 7.8, temperature of 26°C and dissolved ammonia of 0.37 mg/L, the un-ionized ammonia, at 0.018 mg/L would be only slightly less than the recommended limit of 0.02 mg/L.

It has also been recommended (National Academy of Sciences and National Academy of Engineering, 1972) that total ammonia nitrogen (N) in public water-supply sources not exceed 0.5 mg/L. Concentrations of nitrite plus nitrate, reported as nitrogen, of less than 10 mg/L are suggested (EPA, 1976) for public water-supply sources because higher concentrations can cause serious and occasionally fatal poisonings (methemoglobinemia) in infants. Maximum observed concentrations of total ammonia nitrogen and nitrite plus nitrate nitrogen (table 6) during the period 1974-76 were below criteria levels.

It was first noted by Sawyer (1947) in Wisconsin that nuisance algal conditions could be expected in lakes when concentrations of inorganic nitrogen (NH $_3$ + NO $_2$ + NO $_3$ as N) as low as 0.3 mg/L are present in conjunction with as much as 0.01 mg/L of phosphorus.

Not only does the concentration of nitrogen and phosphorus have an important influence on algal growth, but as pointed out by the Technical Advisory Committee to the Secretary of the Interior (Department of the Interior, 1968), "The total nitrogen-total phosphorus ratio is also of importance. The ratio varies with the water, season, temperature, and geological formation, and may range from 1 or 2:1 to 100:1. In natural waters, the ratio is often near 10:1, and this appears to be a good

Table 6.--Mean values and ranges in concentrations of various forms of nitrogen and phosphorus in the French Broad River at Marshall, N.C., 1974-77 water years. (All values in milligrams per liter, except as noted.)

Constituent	Number of samples		Range	
		Mean	Minimum	Maximum
Total nitrite plus nitrate (N)	32	0.60	0.28	2.4
Dissolved nitrite plus nitrate (N)	32	.46	.30	.84
Total ammonia nitrogen (N)	29	.12	.00	.42
Dissolved ammonia nitrogen (NH ₄ as N)	29	.08	.00	.29
Dissolved ammonia (NH ₄)	29	.10	.00	.37
Total organic nitrogen (N)	29	.71	.00	4.0
Dissolved organic nitrogen (N)	29	.26	.00	1.2
Total Kjeldahl nitrogen (N)	32	.83	.00	4.2
Suspended Kjeldahl nitrogen (N)	30	.54	.00	3.8
Dissolved Kjeldahl nitrogen (N)	32	.34	.10	1.2
Total nitrogen (N)	32	1.4	.66	4.8
Total nitrogen (NO ₃)	32	6.3	2.9	21
Total nitrite plus nitrate in bottom deposits (mg/kg)	5	2.9	1.3	6.0
Total Kjeldahl nitrogen in bottom deposits (mg/kg)	5	200	8.0	560
Total phosphorus (P)	32	.22	.03	1.2
Dissolved phosphorus (P)	32	.07	.01	.48
Total orthophosphorus (P)	31	.10	.01	.48
Dissolved orthophosphorus (P)	31	.05	.00	.26
Dissolved orthophosphate (PO ₄)	31	.15	.00	.80
Total phosphorus in bottom material (mg/kg)	4	142	100	240

guideline for indicating normal conditions." Weiss and Kuenzler (1976) support this observation by reporting that ratios of 10-12:1 are indicative of normal conditions in North Carolina lakes. The ratio of nitrogen to phosphorus can be used as an indication of the potential for excess growth of algae. If phosphorus is considered the limiting nutrient, a low ratio suggests that there is sufficient phosphorus for algae to utilize all the available nitrogen for growth, and a high ratio indicates that there is not enough phosphorus for algae to use all the available nitrogen.

Ranges and mean values for nutrient concentrations found at Marshall are shown in table 6. Mean concentrations of nitrogen species are below suggested criteria levels for drinking-water sources; however, the ratio of total nitrogen to total phosphorus for mean concentrations is low enough, at 7:1, to suggest that these waters are susceptible to nuisance algal growths given suitable light and temperature conditions.

Although much remains to be learned about the overall significance of the various forms of nitrogen and phosphorus in water it is expected that both the forms and the mode of transport will eventually be understood to be important in determining the significance of the two elements. Data given in table 6 show that nutrients are transported both in solution and in suspension (total material minus dissolved material equals suspended material). Higher concentrations occur during high flows when the nutrient-rich bottom materials are in active transport. No strong general correlation between stream discharge and nutrient concentrations has been observed (perhaps due partially to seasonal patterns produced by biologic activity and inexactness in some of the analytical methods); but, as shown in figure 7, the amount of nitrogen and its distribution in the aqueous matrix are definitely related to the amount of discharge. Similar patterns of distribution seem to prevail for phosphorus.

Trace Metals

Selected samples collected from 1974 through 1977 were analysed for iron, manganese, arsenic, cadmium, chromium, cobalt, copper, lead, mercury, selenium, and zinc. Table 7 lists the ranges and mean concentrations found for these constituents, along with quality criteria based on EPA guidelines for drinking water. Chromium, lead, selenium, and zinc are the only trace metals to occasionally exceed drinking-water standards. It should be noted that most of these samples were collected during periods of high flow when suspended sediment concentrations were also high. Because all of the metals listed except arsenic, cadmium, selenium and mercury clearly tend to be transported in association with suspended sediment, means of total concentration shown in table 7 are probably biased toward higher values. At the low concentrations

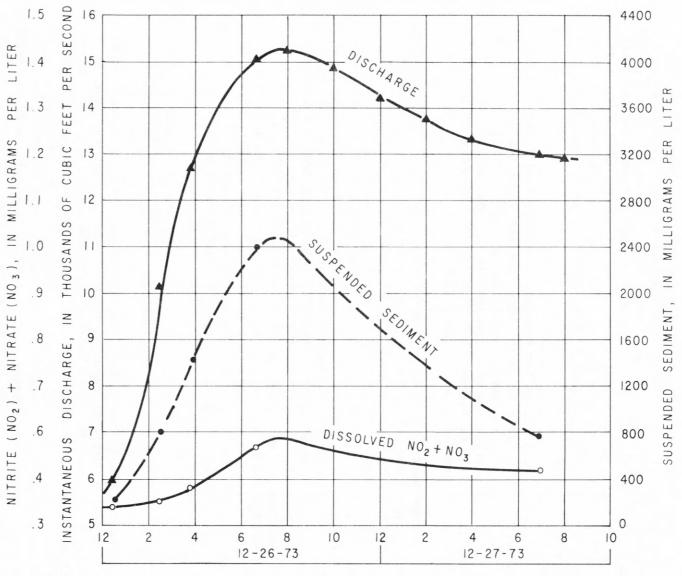


Figure 7.--A comparison of changes in nitrite (NO_2) plus nitrate (NO_3) nitrogen, suspended sediment, and stream discharge with time, French Broad River at Marshall, N.C., December 26-27, 1973.

Table 7.--Trace metal concentrations and associated quality criteria for the French Broad River at Marshall, N.C., 1974-77 water years. Concentrations in micrograms per liter.

Trace metal	Number of samples	Range	Mean ^l	Quality ₂ criteria
Dissolved arsenic	9	0-9	3	50
Total arsenic		0-10	4	50
Dissolved cadmium Total cadmium	9	0-3 0-9	1 3	10 10
Dissolved chromium	34	0-14	2	50
Total chromium	34	0-90	21	50
Dissolved copper	34	0-9	3	1000
Total copper	34	0-230	26	1000
Dissolved iron	34	40-380	128	1000
Total iron	32	410-70,000	15,077	
Dissolved lead	34	0-27	5	50
Total lead	34	0-250	54	200
Dissolved manganese Total manganese	9	0-67 30-640	23 156	200
Dissolved mercury Total mercury	9	0-0.5	0.1 0.1	2 2
Dissolved selenium	9	0-20	7	10
Total selenium		0-29	13	10
Dissolved zinc	34	0-70	14	5000
Total zinc	34	10-6900	327	5000
Dissolved cobalt Total cobalt	9	0-3 0-49	0 12	

Those means based on 9 samples included 4 samples that were collected during high flow. Those means based on 32 and 34 samples included approximately 8 and 9 samples respectively that were collected during high flow.

National Academy of Sciences and National Academy of Engineering, 1972. U.S. Environmental Protection Agency, 1976.

Criteria references:

measured, the mode of transportation of arsenic, cadmium, selenium and mercury is not clearly defined. Arsenic and mercury apparently are carried in solution, selenium seems to be mostly in solution, and cadmium appears to be associated with the sediment.

Biological Characteristics

The systematic collection of biological data began at Marshall in the 1974 water year. The biological parameters analyzed were fecal coliform bacteria, 5-day biochemical oxygen demand (BOD $_5$), chemical oxygen demand (COD), and algal bioassays. Because dissolved oxygen availability influences the survival and diversity of aquatic life and is affected by the BOD and COD as well as temperature, oxygen and temperature are also discussed in this section.

Fecal coliform bacteria are those members of the coliform group found in the feces of various warm-blooded animals, and used as an indicator of bacterialogical pollution. According to U.S. Environmental Protection Agency (1976) criteria, the number of fecal coliform bacteria in bathing waters should not exceed a log mean of 200 colonies per 100 mL (milliliters) based on a minimum of 5 samples in a 30-day period. At Marshall the log mean count for the 1974-77 water years was 1,100 colonies per 100 mL with a range from less than 10 to 12,000 colonies per 100 mL (table 3). Fifty-eight percent of the water samples analyzed exceeded the recommended limit. (Data furnished by North Carolina Department of Natural Resources and Community Development, 1974-1977.) These high counts are usually the product of untreated sewage or animal wastes entering the river system. However, unless fecal streptococci and other bacterialogical pollution indicators are measured in connection with fecal coliform, it is impossible to distinguish whether the bacterial pollution is from human or animal sources.

Just as oxygen in the air is necessary for the respiration of airbreathing organisms, so too is dissolved oxygen necessary in water to support many forms of aquatic life. The saturation concentration of dissolved oxygen varies inversely with temperature, and as shown in figure 8, will range from 13.7 mg/L to 7.9 mg/L over the range of daytime water temperature that has been measured at Marshall (table 3). A minimum concentration of 5.0 mg/L of dissolved oxygen has been recommended (EPA, 1976) as a criteria level necessary for maintenance of a varied population of fish and other aquatic organisms, whereas 4.0 mg/L is cited as the minimum concentration that will support a variety of tolerant species. It should be noted, however, that dissolved oxygen levels below 5.0 mg/L will not necessarily result in fish kills, especially if the depleted oxygen levels last only for brief periods.

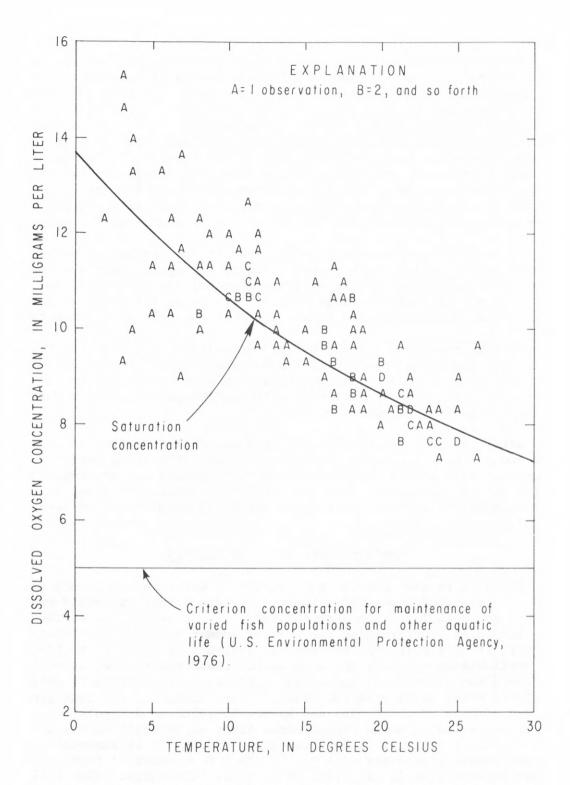


Figure 8.--Dissolved oxygen concentration versus water temperature, French Broad River at Marshall, N.C., 1974-77 water years.

Under natural conditions, water temperatures follow ambient air temperatures but are buffered from extreme values of air temperature by the slower heating and cooling rates of the water. During the summmer months, high temperatures reduce the solubility of oxygen in water. Consequently, evaluation of dissolved oxygen levels in streams is important for the critical high temperature months. As shown in figure 8, the dissolved oxygen concentrations in the French Broad at Marshall are high year-round, remaining near or above the saturation level even at higher temperatures. The lowest reported dissolved oxygen concentration (table 3) (North Carolina Department of Natural Resources and Community Development) during the 1974-77 water years was 7.3 mg/L.

Biological uptake of oxygen dissolved in the stream, as measured by the BOD_5 test, is low, with a mean value of 2.0 mg/L. Available oxidizable organic material, measured by the chemical oxygen demand test (COD), is greater, with a range of 10-56 mg/L. Overall, the oxygen level tests characterize the French Broad at Marshall as a clean river.

A rough measure of biological productivity is given by the rate of periphyton growth on an artificial substrate. Discontinuous data (fig. 9) show that growth rates are generally low with a tendency for a seasonal variation in productivity with maximum growth rates occurring during the spring and summer months.

Algal bioassays (table 8) suggest a seasonal distribution of dominant groups with cyanophyta (blue-green algae) prevailing during the summer and fall months, while chrysophyta (diatoms) appear prominantly during winter and spring. The low algal cell counts and group distribution (table 8) indicate that algae are not a problem in the stream.

Man's Effects On Water Quality

Compared to many rivers, the quality of water in the French Broad River is very good. However, there is evidence that virtually every quality characteristic has deteriorated as man's activities in the basin have increased. Determining the precise amount of this deterioration, however, is difficult. A few chemical analyses of water from this river are available as early as the 1920's, but these are too few in number and there was already too much human activity by the 1920's to define undefiled water quality in the river. J. C. Ramage of the Southern Railway Company reported (Ray and Randolph, 1928) an analysis of a sample collected from the French Broad River at Marshall on May 3, 1923, at a discharge believed to be about $2,500 \text{ ft}^3/\text{s}$. It is interesting to compare Ramage's analysis with one by the U.S. Geological Survey on a sample collected April 12, 1976, at a similar discharge. (See table 9.) Differences in conventions of reporting results and refinements in analytical techniques make a rigorous comparison of the two analyses

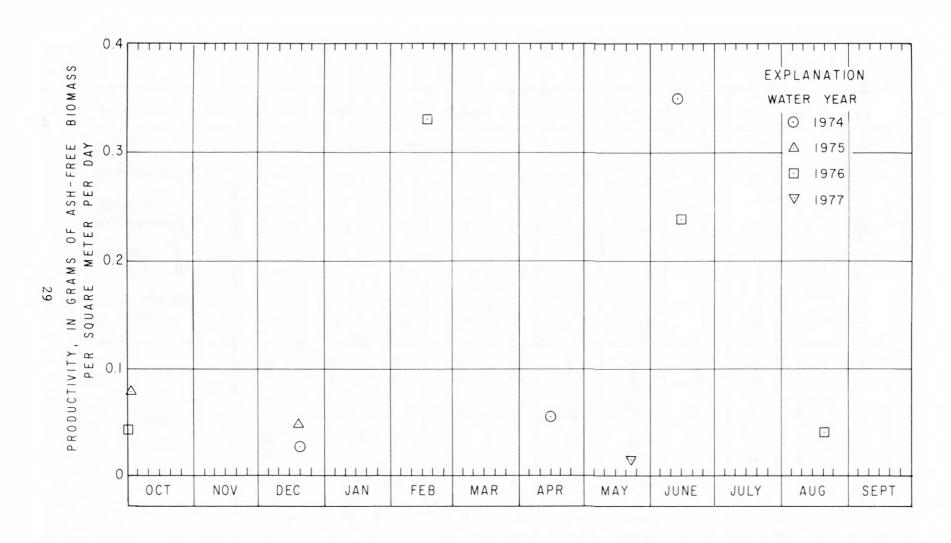


Figure 9.--Periphyton productivity in the French Broad River at Marshall, N.C., 1974-77 water years.

Table 8.--Algal bioassays, in percent of total cell count and the total cell count, for the French Broad River at Marshall, 1974-77 water years

			Date of	f sample	and pe	ercent of	f total o	cell cour	nt		
	1974	1974	1974	1975	1975	1976	1976	1976	1976	1977	1977
Group	15,	14,	2,	6	1,	17,	15,	20,	16,	28,	23,
	Apr.	June	Oct.	June	Oct.	Feb.	June	Aug.	Dec.	Mar.	May
Cyanophyta (Blue-green)	86	83	51	54			58	58		5	
Chlorophyta (Green)		7	23	2	6		8	30		3	
Chrysophyta (Diatoms)		9	18	44	94	97	32	12	99	92	92
Euglenophyta						2					8
Other	14	1	8			1	2		1		
Total cell count	1,700	5,000	1,700	1,900	250	1,700	1,700	5,500	690	830	860

Table 9.--Comparison of chemical analyses of water from the French Broad River at Marshall, N.C., 1923 and 1976

	Concentrations in mil	ligrams per liter		
Dissolved constituent	¹ May 3, 1923 (discharge estimated at 2500 ft ³ /s)	April 12, 1976 (discharge = 2530 ft ³ /s)		
Total dissolved solids	68	44		
Dissolved solids sum	33.40	44		
Silica (SiO ₂	.86	10		
Iron (Fe)	1.08	0.89		
Calcium (Ca)	6.92	4.2		
Magnesium (Mg)	.54	.2		
Sodium (Na)	2.20	7.0		
Potassium (K)	.93	1.0		
Carbonate (CO_3)	5.60	.0		
Bicarbonate (HCO_3)		15		
Sulfate (SO ₄)	11.90	11		
Chloride (C1)	2.68	2.8		
Nitrate $(N0_3)$	trace	.32		
Total hardness	19.55	11		
Alkalinity	9.3	12		

¹Taken from Ray, C. E. and Randolph, E. E., 1928

impractical. However, the overall impression is that, under low-to-medium high flow conditions, the quality of water in 1976 is similar to what it was in 1923, although the population and general development of the basin have certainly increased greatly since then. Ray and Randolph (1928) mentioned a number of industries, particularly several tanneries, that are no longer in operation. Thus, decreases in certain types of pollution sources, plus increased attention to waste treatment and disposal practices, have probably combined to minimize further deterioration in water quality over the past 50 years.

In the absence of data needed to make a direct evaluation of man's influence on the quality of North Carolina's larger rivers, Wilder and Simmons (1978) proposed that natural water-quality characteristics be estimated on the basis of the quality of water in environmentally similar unpolluted drainage areas. Such areas are usually in headwater areas and difficult to find, but ll sites were found in the western part of the State which seem to represent unpolluted or baseline conditions except for pollutants brought in through the air and with precipitation (C. E. Simmons, U.S. Geological Survey, written commun., 1978). These baseline sites are shown in figure 10, along with a list of station names and locations. These sites were sampled an average of four times each during 1973-77 for the purpose of determining the quality of ground-water inflow to streams (low flow) and intense runoff following storms (high flow). A summary of these analyses, shown in table 10, indicates very little difference between the quality of water at low and high flows. This tendency toward sameness is undoubtedly a result of the sparingly soluble nature of the igneous and metamorphic rocks that underlie the area and the fact that ground-water recharge in the upland areas is shunted laterally through fractures in the rocks to points of discharge less than 1 mile (and commonly less than one-half mile) from their point of arrival at the water table (LeGrand, 1958, p. 179).

Table 10 also shows a comparison of water quality at baseline sites with samples taken from the French Broad River at Marshall during periods of distinct low flow and high flow. The differences between the two sets of samples are believed to closely approximate the quantitative effects of man's activities on water quality at Marshall.

The gross effects of man's activities on water quality can best be evaluated in terms of the mass transport of materials by the streams. The loads of substances contributed by pollution can be estimated as described by Wilder and Simmons (1978), using the estimates of natural-quality concentrations (table 10) to calculate estimated natural loads. These natural-load estimates are subtracted from the actual loads determined from the samples collected at Marshall and the differences between the two are assumed to represent inputs resulting from man's activities. It should be emphasized that computation of representative transport loads requires both continuous streamflow measurements and water quality measurements made with sufficient frequency to allow the

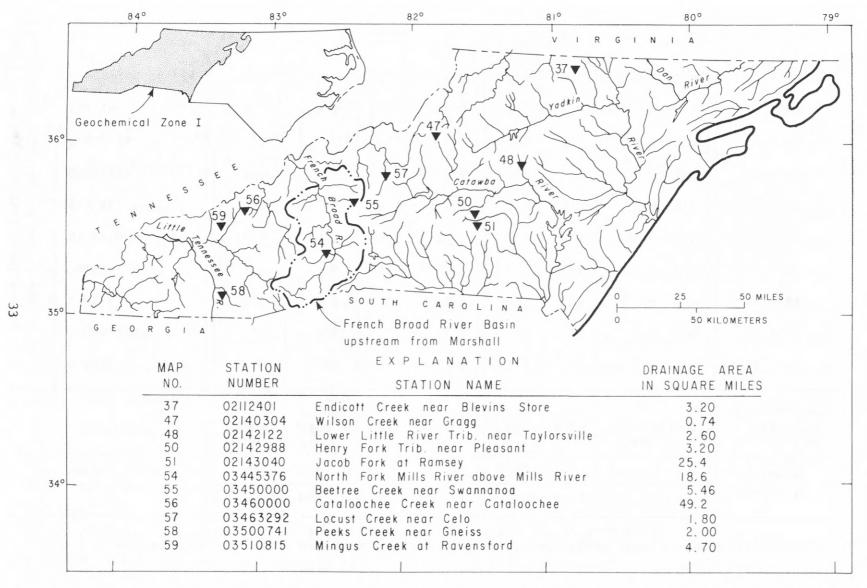


Figure 10.--Location of baseline water-quality sampling sites in Geochemical Zone I (from C. E. Simmons, U.S. Geological Survey, written commun., 1978).

Table 10.--Comparison of water quality of samples from the French Broad River at Marshall, N.C., with samples from baseline-quality sites in the same area

		French	Broad Riv	er at Marshall	Base	line qua	ality sites	Range in
		Mean	value	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	Mean value			percent attributable
		Low flow (<1800 ft ³ /s)	High flow (>1800 ft ³ /s)	Range of all samples		to pollution based on mean values ^a		
	Calcium	7.0	4.6	3.2 - 10.0	1.3	1.3	0.5 - 3.0	72 - 81 ^b
Ø	Magnesium	1.2	1.1	.2 - 2.0	.6	. 4	.3 - 0.9	50 ^b - 64
constituents per liter)	Sodium	14.0	5.8	2.4 - 22.0	1.5	.8	.4 - 2.2	86 - 89 ^b
stit lite	Potassium	1.7	1.6	1.0 - 2.9	1.0	.6	.3 - 1.9	41 ^b - 62
con	Bicarbonate	26.0	15.0	9.0 - 35.0	7.4	5.1	2.0 - 9.5	66 - 72 ^b
lved	Sulfate	24.0	11.0	5.1 - 42.0	2.2	2.2	.8 - 5.7	80 - 91 ^b
isso ligr	Chloride	4.3	3.0	.9 - 5.8	0.9	.7	.0 - 2.0	77 - 79 ^b
Major dissolved (milligrams	Fluoride	.1	.2	.0 - 1.2	0.1	0.1	.0 - 0.5	0 ^b - 50
Maj	Silica	10.0	8.2	3.7 - 11.0	8.1	6.6	3.5 - 9.4	19 ^b - 20
	Dissolved Solids	76.0	44.0	30.0 - 112.0	19.0	15.0	12.0 - 22.0	66 - 75 ^b

	Total Nitrogen	1.2	1.5	0.66 - 4.8	0.19	0.30	0.0 - 0.92	80 - 84 ^b
is tms	Organic Nitrogen	.50	.79	.0 - 4.0	.11	.13	.0 - 0.29	78 ^b - 84
ients igrams liter)	Nitrate Nitrogen	5.2	6.8	2.9 - 21.0	.08	.17	.0 - 4.0	98 - 98
Nutrients (milligrams per liter)	Ammonia Nitrogen	.13	.11	.0 - 0.42	.0	.01	.0 - 0.01	91 - 100 ^b
	Total Phosphorus	.16	.24	.03 - 1.2	.01	.01	.0 - 0.02	94 ^b - 96
	Total Arsenic	.33	5.2	.0 - 10.0	.1	.0	.0 - 1.0	70 ^b - 100
r)	Total Chromium	12.0	24.0	.0 - 90.0	10.0	10.0	1.0 - 20.0 ^c ,d	17 ^b - 58
; liter)	Total Copper	11.0	32.0	.0 - 230.0	4.0	4.0	.0 - 13.0	64 ^b - 88
Trace Metals rograms per	Total Iron	958.0	20,602	410 - 70,000	460.0	1800.0	20 - 8600 ^e	52 ^b - 91
ace Me grams	Total Lead	41.0	58.0	.0 - 250.0	5.0	9.0	.0 - 25 ^{c,d}	84 - 88 ^b
Trac	Total Mercury	.17	.12	.0 - 0.5	.10	.10	.0 - 0.50	17 - 41 ^b
(mic	Total Selenium	5.0	17.0	.0 - 29.0	.0	.0	.0 - 0.0 ^{c,d}	100 - 100
	Total Zinc	58.0	424.0	10.0 - 6900.0	10.0	10.0	.0 - 40.0 ^d	83 ^b - 98

^aSome constituents have a higher percent attributable to pollution at high flow whereas others have a higher percent attributable to pollution at low flow.

bLow flow.

^CExceeded limits recommended in <u>Safe Drinking Water Act</u>, Federal Register, Dec. 24, 1975, in some samples.

d Exceeded limits recommended in <u>Quality Criteria for Water</u>, U.S. Environmental Protection Agency, 1976 in some samples.

^eNo recommended limits.

determination of continuous concentration data. The frequency with which concentrations of transported materials must be measured varies with the variability of the constituent being measured, but the computation of usefully accurate loads usually requires at least daily values. As discussed earlier in this report, the only daily water quality measurement made in this investigation is specific conductance. Thus, it is possible to estimate pollution loads only for those constituents that correlate meaningfully (correlation coefficient greater than 0.75) with specific conductance. (See table 4.) A summary of the amounts and sources of selected major dissolved constituents transported by the French Broad River at Marshall, calculated as described above, is shown in table 11.

Table 11.--Sources and average amounts of major dissolved constituents transported by the French Broad River at Marshall, N.C., 1974-77 water years

Constituent	Total load (tons/yr)	Natural load (tons/yr)	Pollution load (tons/yr)	Percent attribut- able to pollution
Sodium	22,900	3,630	19,200	84
Bicarbonate	49,500	19,100	30,500	62
Sulfate	37,200	6,340	30,900	83
Dissolved Solids	147,000	51,300	95,800	65

The estimates of the effects of man on the quality of water at Marshall shown in table 11 are based on several assumptions (Wilder and Simmons, 1978), the most important of which is that natural quality of water in a large river is essentially the same as that in a small stream if their natural environments are the same. There is, of course, no direct way of evaluating the validity of this assumption. For the French Broad River, however, some degree of the amount of confidence to be placed in the methodology used can be derived by comparing the results of the areal estimates derived from the baseline-quality network with results from a daily station operated on Cataloochee Creek near Cataloochee, N.C. (Shown as map number 56 in figure 10.)

At the station, Cataloochee Creek has a drainage area of 49.2 mi², all of which lies in a remote section of the Great Smoky Mountains National Park. On the basis of topography, geology and climate, the

Cataloochee basin is hydrologically very similar to that of the French Broad basin at Marshall, and both lie entirely within Geochemical Zone I (fig. 10). Except for a one-lane access road and a sparse network of hiking trails and bridle paths, the Cataloochee basin is completely undeveloped; and activity within it is limited to this type of recreation, plus a small amount of overnight camping. Virtually all use of the basin occurs in the summer months. Although slight increases in nutrients and suspended materials were noted during peak-use periods, major dissolved chemical constituents were not noticeably affected.

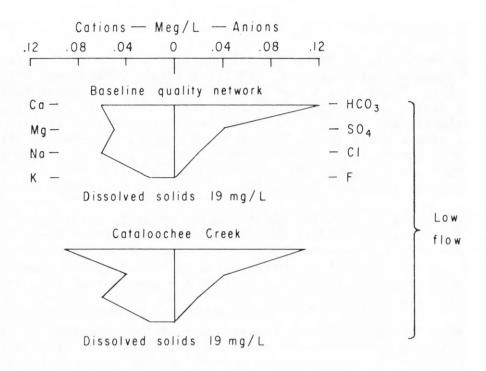
With respect to major constituents, water in Cataloochee Creek should approximate natural quality in the French Broad River basin. The marked similarity between the chemical character of water in Cataloochee Creek and more general estimates based on miscellaneous samples from much smaller basins $(0.74-18.6~\rm mi^2)$ in the baseline-quality network is shown in figure 11.

An additional check on the adequacy of the baseline-quality network in furnishing valid information on natural quality at sites where such quality cannot be measured directly can be made by comparing natural loads for the French Broad River estimated by use of the baseline-quality network with those computed from daily measurements at Cataloochee. The results obtained for annual total dissolved solids are shown in table 12 as unit loads in order to facilitate comparison of the data.

Table 12.—Comparison of natural dissolved-solids unit loads estimated for the French Broad River at Marshall, N.C., with unit loads calculated from daily measurements for Cataloochee Creek near Cataloochee, N.C.

Dissolved-Solids	Unit	Loads	(tons	per	million	cubic	feet
		of dis	charge	2)			

Water year(s)	French Broad River at Marshall (estimated from baseline-quality network)	Cataloochee Creek near Cataloochee			
1974	0.57	0.61			
1975	0.57	0.52			
1976	0.54	0.55			
1977	0.53	0.65			
1974-77	0.55	0.56			



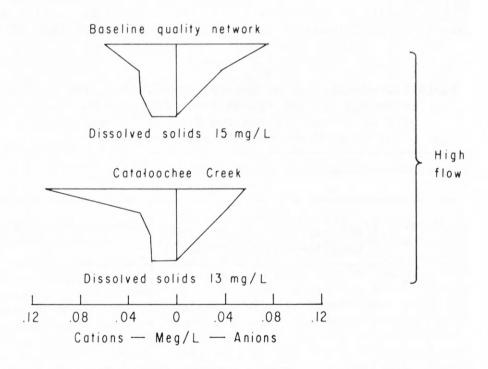


Figure 11.—Natural chemical character and dissolved solids in the French Broad River basin as estimated from the baseline water-quality network compared to measurements at Cataloochee Creek near Cataloochee, N.C., 1974-77 water years (diagram pattened after Stiff, 1951).

Comparisons based on actual loads can be misleading since, as with concentration, they are dependent upon the amount of streamflow. Because of differences in streamflow at the two stations, a more realistic means of comparing loads is by converting the actual loads to some equivalent unit value (in this case, unit load of dissolved solids in tons per million cubic feet of discharge). This technique is also useful for reducing the year to year effects of changing streamflow, for as will be seen in the Trends section of this report, significant trends can be masked by the "noise" of unusually wet or dry years.

The close agreement of the character and amount of natural dissolved matter estimated for the French Broad River at Marshall with that measured for a similar environment at Cataloochee offers encouraging evidence that the baseline-quality network is furnishing reliable baseline data for evaluating the effects of man's activities on water quality of the French Broad River.

To give the information shown in table 11 a somewhat broader perspective, historical data were used to calculate annual dissolved solids loads for the period of record at Marshall. The results, which are in table 13, show that during the periods 1958-67 and 1974-77, dissolved solids transport ranged from 131,000 tons/yr to 184,000 tons/yr, and that from 61 to 75 percent of this load was due to pollution. In general, pollution loads are greater during years of high total discharge even though concentrations of major dissolved constituents invariably decrease during high flows. The greater pollution loads during high-flow years probably reflect the influence of non-point source inputs on the quality of water in the river, because other factors being equal, point-source pollution input is probably largely independent of streamflow over a year's time.

The chemical character of inorganic pollution inputs to the river is illustrated in figure 12, which shows diagrams of natural water quality superimposed on diagrams of the average quality of high and low flow samples from the river (table 10). These diagrams show that non-natural inputs dominated most major dissolved ionic species, with the greatest increases occurring in sodium (Na), calcium (Ca), sulfate (SO_4), and bicarbonate (HCO_3).

Trends

A major concern in modern water-quality programs is the rate at which the quality of streams may either be deteriorating or improving. Thus, several investigations by both State and national agencies have the stated objective of detecting trends in stream quality. Detecting such trends, however, is difficult; and much of the effort currently being expended for this purpose may prove unsuccessful. Among the most troublesome problems encountered in detecting trends are the so-called

Table 13.--Dissolved solids loads, French Broad River at Marshall, N.C., 1958-67, 1974-77 water years

	Measured at Marshall		Estimated from baseline-quality network		Loads			Unit loads		
	A	В	C	D	E	F	G	Н	I	J
Water year	Total discharge (million cubic feet/yr.)	Total dissolved solids (tons/yr)	Dissolved solids in ground water (tons/yr)	Dissolved solids in overland flow (tons/yr)	Dissolved solids in natural load (tons/yr) C + D	Dissolved solids in pollution load (tons/yr) B - E	Percent of total load from pollution (F/B) x 100	Total unit load (tons/million cubic feet) B/A	Natural unit load (tons/million cubic feet)	Pollution unit load (tons/million cubic feet) H - I
1958	89,360	143,000	40,800	10,400	51,200	91,800	64	1.60	0.57	1.03
1959	66,010	131,000	30,100	7,700	37,800	93,200	71	1.99	.57	1.43
1960	92,720	153,000	42,200	10,700	52,900	100,100	65	1.64	.57	1.07
1961	79,150	142,000	36,100	9,200	45,300	96,700	68	1.80	.57	1.23
1962	94,040	165,000	42,900	10,900	53,800	111,200	67	1.76	.57	1.19
1963	62,670	142,000	28,600	7,300	35,900	106,100	75	2.26	.57	1.69
1964	77,380	154,000	35,200	9,000	44,200	109,800	71	2.00	.57	1.43
1965	104,140	180,000	47,500	12,100	59,600	120,400	67	1.72	.57	1.15
1966	69,270	152,000	31,600	8,000	39,600	112,400	74	2.19	.57	1.62
1967	84,620	152,000	38,600	9,800	48,400	103,600	68	1.79	.57	1.22
1974	101,570	184,000	46,300	11,800	58,100	125,900	68	1.81	.57	1.24
1975	96,800	150,000	44,100	11,200	55,300	94,700	63	1.55	.57	0.98
1976	92,270	130,000	37,200	13,000	50,200	79,800	61	1.41	.54	0.87
1977	78,440	125,000	20,800	20,800	41,600	83,400	67	1.59	.53	1.06

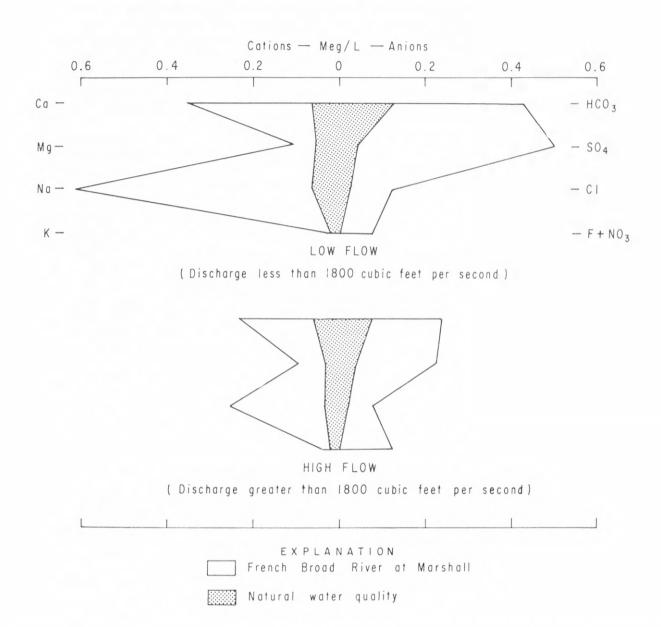


Figure 12.—Differences in chemical character between estimated natural water-quality and actual average quality for samples taken from the French Broad River at Marshall, N.C., during high and low flow (diagram patterned after Stiff, 1951).

"noise" effects of short-term variations caused by variations in environmental conditions, particularly variations in streamflow. In addition, the trends themselves also are not necessarily constant over long periods of time. This is often due to the fact that different aspects of water quality may change in response to factors not related to environmental conditions. For example, the discharge of manufacturing wastes may increase or decrease with changes in the economy.

If water-quality data were available over sufficiently long periods of time, natural trends caused by long-term changes in weather patterns would probably be detectable within them. However, uninterrupted water-quality records are seldom collected for periods lasting more than a few years, and any systematic variations during these periods almost certainly are caused by changes in man's activities. Thus, the search for trends can be made simpler by concentrating on man's effects on quality rather than on the combined effects of both man and nature. For the French Broad River at Marshall, selected water-quality data are available on a daily basis for 1958-67 and 1974-77. (See figure 2.) For the earlier period, only information concerning major dissolved inorganic constituents was collected, and comparisons of modern data with historical data must be based on measurements of these constituents.

A first step in the search for trends is to deduce what factors are likely to have significantly influenced variations in water quality, and what the general influence of these factors might have been. In the French Broad River basin four factors are suspected to have dominated the water-quality of the river during the period of study:

- 1. Variations in stream discharge are known to cause short-term variations in constituent concentrations that, over periods as long as two years, may mask variations in water quality due to other causes. For example, increases in pollutant transport during years of high flow are believed to reflect in part, increases in the amounts of non-point source pollution.
- 2. The population of the basin has increased at an annual rate of slightly more than one percent. This increase should cause small increases in most major chemical constituents.
- 3. Manufacturing employment (and therefore industrial output) has increased steadily even if somewhat erratically on an annual basis. Unless other factors such as changes in manufacturing processes or application of pollution abatement techniques are involved, there should be a general relation between manufacturing employment and point-source pollution input to the river.

4. Changes in waste-treatment facilities and manufacturing processes usually have an effect on water quality. During the most recent sampling period (1974-77) such changes apparently have resulted in improved water quality, and modification of previous trends. Although these changes are known to take place, there is presently no reliable way of documenting all these changes, or more particularly, assessing the impact of the changes.

A preliminary appraisal of the effects of these factors on chemical quality may be made by comparison of simultaneous plots of pollution loads of dissolved constituents and the three measurable factors thought to contribute to them. Figure 13 shows simultaneous time plots of stream discharge, manufacturing employment, population, and dissolved—solids pollution load. The general impression is that from 1958, when water-quality data collection began, through 1967, when data collection was suspended, dissolved pollution loads increased as did population and manufacturing. Pollution loads responded to variations in discharge also. A multiple-regression analysis for the period of record indicated that a major part of the variation in dissolved pollution loads was related to variations in discharge and manufacturing employment, with population playing a relatively minor role.

Figure 13 also suggests that from the resumption of sampling in 1974 through 1977 a decreasing trend in pollution loads was in progress. This trend is probably associated, at least in part, with the discontinuance of a major rayon-producing facility midway in the 1975 water year.

Information on which chemical characteristics are most likely to contribute to trends is also helpful in establishing focal points for trend analyses. The chemical equivalents diagrams shown on figure 12 indicate that at high flows input of pollutants to the French Broad is fairly well balanced among the major chemical species. At low flows, however, sodium and sulfate increase greatly, suggesting that they are principal components of point-source pollution input. The increases in calcium and bicarbonate show them to be secondary pollutants.

To further explore the chemical character of man-made inputs to the river, the annual means for analyses of samples collected during low flow were plotted on a trilinear chemical equivalent diagram as shown in figure 14. This diagram indicates a time-related shift from a predominately sodium-sulfate-type pollution input in 1958 toward an input more evenly balanced between calcium, sodium, bicarbonate, and sulfate in 1977. Because of the discontinuity in data collection from 1967 to 1974, it is not possible to determine precisely when these shifts in chemical character began, but the transition seems to have been occurring when sampling was resumed in October 1973.

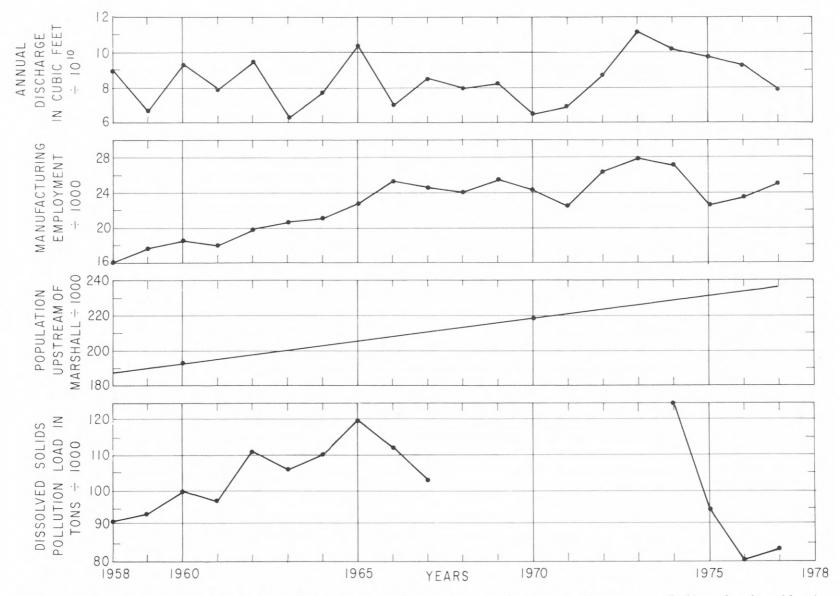


Figure 13.--Stream discharge, manufacturing employment, population estimates, and dissolved pollution loads, French Broad River at Marshall, N.C., 1958-77 water years.

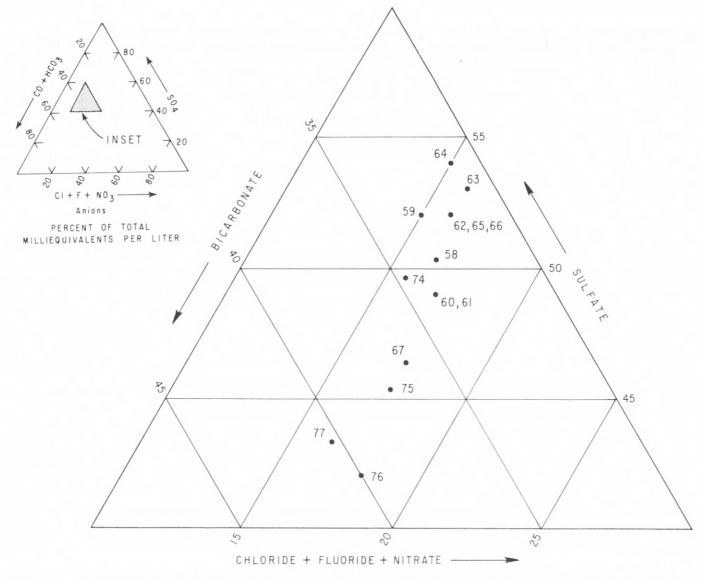


Figure 14.--Trilinear diagram of annual means for analyses of samples collected during low flow, French Broad River at Marshall, N.C., 1958-67, 1974-77 water years (diagram after Piper, 1944).

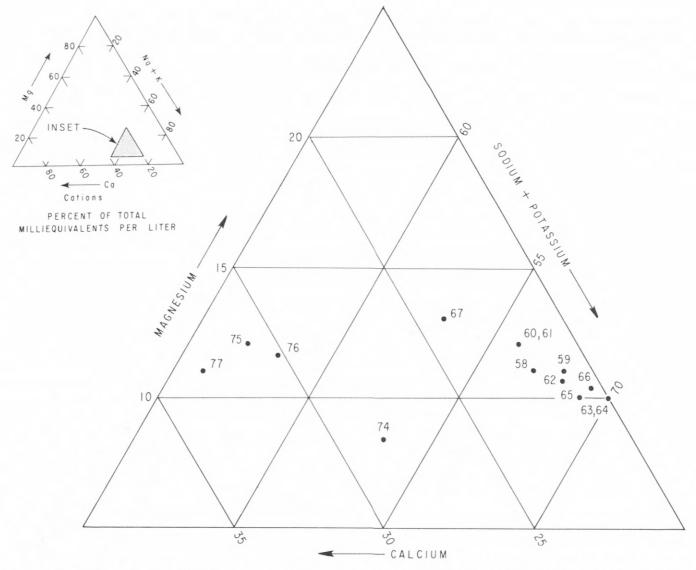


Figure 14.--Trilinear diagram of annual means for analyses of samples collected during low flow, French Broad River at Marshall, N.C., 1958-67, 1974-77 water years (diagram after Piper, 1944)--Continued

To investigate further, annual loads of the major conservative ionic species in solution (sodium, calcium, and sulfate) were regressed individually as dependent variables against both discharge and manufacturing employment as independent variables. Correlation coefficients resulting from these regressions are shown in table 14. From this table it seems apparent that during the earlier sampling period sodium varied primarily in response to variations in manufacturing employment, whereas calcium responded most sensitively to changes in discharge. Sulfate also was most responsive to discharge, but showed some response to manufacturing employment as well.

Table 14.—Correlations of major dissolved ionic species with stream discharge and manufacturing employment for the French Broad River at Marshall, N.C., 1958-67, 1974-77 water years

Independent variable		1958-67		1974-77				
		ndent var		Dependent variable Correlation coefficients				
	Sodium	Calcium	Sulfate	Sodium	Calcium	Sulfate		
Stream discharge	.16	.92	.92	.74	.94	.72		
Manufacturing employment	.77	.29	.61	.73	.43	.71		

Although only four years of data are available for the most recent sampling period (1974-77), it is interesting to compare regression analyses for this period with those for the earlier period. Pollution loads of sodium and sulfate now seem to be about equally correlatable with discharge and manufacturing, while calcium is still dominated by discharge. The apparently decreased influence of manufacturing on sodium and sulfate is consistent with observations of changes in the chemical character of pollution input to the river discussed earlier.

A summary of trends in inorganic pollution input to the French Broad, as represented by a few inorganic constituents, is illustrated in figure 15 which shows average unit pollution transport, in tons per million cubic feet of discharge, for two 5-year periods during the earlier sampling period, and for the most recent 4-year period. It appears that even with continued economic growth the inorganic chemical quality of the river has improved, in most, but not all respects, since sampling was first discontinued in 1967. From information gathered from public officials and furnished by manufacturers in the basin, it seems likely that this improvement is a result of both efforts to improve waste-treatment methods and efforts to clean up particularly so-called "dirty" manufacturing processes. There is, of course, no way of predicting with certainty what the future trends in the quality of water in the French Broad River will be. At present it appears that a noticeable level of improvement has been attained as the result of a lengthy and expensive effort on the part of public and private interests to return the river to a desirable water-quality condition.

The results are encouraging because they show that the quality of water in our large rivers need not deteriorate continually in the face of economic growth. However, even during the most recent year for which records are available (1977 water year), 67 percent of the total dissolved material transported by the river was attributable to man's activities. (See table 12.) Therefore if, as seems certain, industrial growth in the basin continues, pollution abatement efforts must continue to keep pace. Otherwise, the French Broad River will enter another period of gradual degradation.

Summary

An investigation of the quality of water in the French Broad River at Marshall, N.C., has defined variations in water quality, determined the degree to which the quality of water in the river is affected by man's activities, and analyzed trends in the chemical quality of the river during the period 1958-77. The French Broad River drains 1,667 square miles of the Blue Ridge Mountains Province in western North Carolina, an area of rugged topography with altitudes ranging from 6,419 feet along the northeastern drainage divide to 1,240 feet where the river enters Tennessee. The drainage area upstream from Marshall is 1,332 square miles.

The French Broad River is the most industrialized river basin in the mountain region of the State with about 30 percent of the employed population engaged in the manufacture of textiles, pulp and paper, leather goods, furniture and other wood products. Population in the basin above Marshall has increased 40 percent between 1940 and 1970 to approximately 218,000 inhabitants.

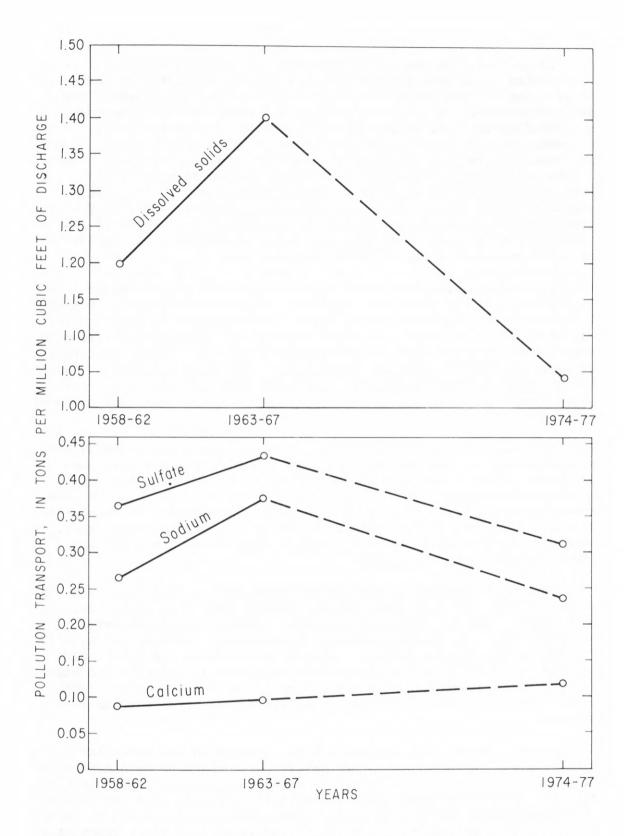


Figure 15.--Inorganic pollution transport for selected constituents, French Broad River at Marsall, N.C.

In general, the quality of the water in the French Broad River as represented by samples taken at Marshall is satisfactory for most purposes. None of the major dissolved constituents and nutrients, nor defined properties such as hardness, alkalinity and color, exceed limits suggested by the U.S. Environmental Protection Agency for drinking-water sources. Of the trace metals determined, only chromium, lead, selenium, and zinc occasionally exceeded approved drinking-water values. Dissolved oxygen concentrations are high year-round, remaining near or above the saturation level even at higher summer temperatures. Low levels of chemical oxygen demand (COD) and biological oxygen demand (BOD₅) characterize the French Broad at Marshall as a clean river. However, 58 percent of samples analyzed for fecal coliform bacteria during 1974-77 exceeded recommended limits for bathing waters.

Several variations of water quality have been identified and quantified. Of the three most important, the most fundamental has been to determine the extremes within which concentrations of constituents may be expected to range. A second has been to quantify variations in constituent concentration, in particular dissolved ionized constituents, by correlation with specific conductance. The third has been to identify the water-quality variations associated with variations in streamflow. Changing streamflow is perhaps the single most important cause of water-quality variation.

Many major dissolved constituents in the river, particularly dissolved solids, sodium and sulfate, vary linearly with specific conductance. These relations have been quantified by linear regression analysis. However, the relation of specific conductance to streamflow is a non-linear inverse relation, and, as might be expected because of the way that dissolved constituents correlate with specific conductance, concentrations of dissolved constituents also follow a non-linear inverse relation to streamflow.

Suspended sediment concentrations generally increase with increasing streamflow and most trace metals clearly tend to be transported in association with the suspended sediment. At the low concentrations measured, the mode of transportation for arsenic, cadmium, selenium and mercury is not clearly defined. Arsenic and mercury are apparently carried in solution, selenium seems to be mostly in solution and cadmium appears to be associated with the sediment. No strong general correlation between stream discharge and nutrient concentrations has been observed.

Man's activities in the basin have resulted in deterioration of water quality in the French Broad River. By comparison with data from sites thought to represent natural conditions, it is estimated that at the time continuous water-quality monitoring began in 1958, 64 percent of the dissolved-solids load in the river at Marshall was due to pollution. Time-trend analysis shows that from 1958 to at least sometime in

1967 dissolved constituents carried in the river increased, coinciding with general increases in population and industrial employment. The total dissolved-solids load, along with the dissolved sodium, sulfate and calcium loads showed the most dramatic increases. By 1966, 74 percent of the total dissolved load could be attributed to pollution. The exact time that conditions in the river began to improve is not certain because water quality monitoring was discontinued between 1968 and 1973; however, since 1974 the amount of inorganic constituents has decreased dramatically in spite of increased population and industrial growth. New waste-water treatment facilities and improved industrial technology apparently have combined to curb pollution and reverse the earlier trend. In 1977 water quality had returned at least to levels of 1958. It appears that a noticeable level of improvement has finally been attained as the result of a lengthy and expensive effort to return the river to a desirable water-quality condition.

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